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(54) NEGATIVE TYPE RESIST COMPOSITION FOR ELECTRON BEAM OR X-RAY

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide a negative type resist composition for electron beam or X-rays excellent in uniformity of coating on the surface of a substrate and suppressing the occurrence of defects in development.

SOLUTION: The negative type resist composition for electron beam and X-rays contains a crosslinker which causes a crosslinking reaction under the action of an acid and a mixed solvent containing at least one selected from the group (a) comprising propylene glycol monoalkyl ether carboxylates and at least one selected from the group (b) comprising propylene glycol monoalkyl ethers, alkyl lactates and alkyl alkoxypropionates and the group (c) comprising  $\gamma$ -butyrolactone, ethylene carbonate and propylene carbonate. The crosslinker is a phenol derivative containing 3-10 benzene ring forming atomic groups and the molecular weight is  $\leq 2,000$ . The derivative has one or more hydroxymethyl groups and one or more alkoxyethyl groups in one molecule and these groups bond to at least one of the benzene ring forming atomic groups.

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LEGAL STATUS

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2.\*\*\*\* shows the word which can not be translated.

3.In the drawings, any words are not translated.

## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the negative-resist constituent used suitable for super-micro lithography processes, such as a VLSI and manufacture of a high capacity microchip, or other photofabrication processes. It is related with the negative-mold chemistry multiplier system resist constituent which can be used especially suitable for micro processing of the semiconductor device using high energy lines, such as an electron ray, about the negative-mold chemistry multiplier system resist constituent which was made highly minute in more detail using an X-ray, an electron ray, etc. containing excimer laser light and which can carry out pattern formation.

[0002]

[Description of the Prior Art] the integrated circuit is raising the degree of integration increasingly, and consists of the line breadth below a half micron in manufacture of semi-conductor substrates, such as a VLSI, — processing of a detailed pattern has overly come to be needed. In order to fulfill the need, operating wavelength of the aligner used for photolithography is short-wave-ized increasingly, and by the time far-ultraviolet light and excimer laser light (XeCl, KrF, ArF, etc.) are examined, now, it will become. Still more detailed pattern formation has come [ furthermore, / by the electron ray or the X-ray ] to be considered.

[0003] Especially as for an electron ray or an X-ray, the next generation or development of the negative resist which is positioned as a generation's pattern formation technique one after another, and can attain high sensitivity and a high resolving and rectangle profile configuration is desired. Electron-beam lithography emits energy in the atom with which the accelerated electron ray constitutes a resist ingredient, and the process in which collision dispersion is caused, and exposes a resist ingredient. Although

rectilinear-propagation nature increases by using the high-accelerated electron ray, the effect of electronic dispersion decreases and the pattern formation of a rectangle configuration becomes possible by high resolving, on the other hand, the permeability of an electron ray will become high and sensibility will fall. Thus, in electron-beam lithography, sensibility, and definition and a resist configuration had the relation of a trade-off, and the technical problem how it might be compatible in this occurred.

[0004] Conventionally, various proposals have been made [ NEGAREJISUTO / chemistry magnification mold ] about the acid generator. To JP,8-3635,B, an organic halogenated compound at JP,2-150848,A and JP,6-199770,A Iodonium salt, Sulfonium salt to JP,2-52348,A, JP,4-367864,A, and JP,4-367865,A Cl, The acid generator containing Br to JP,4-210960,A and JP,4-217249,A Diazo disulfon, The sulfonate compound is indicated by a diazo sulfone compound and JP,4-226454,A at a triazine compound, JP,3-87746,A, JP,4-291259,A, JP,6-236024,A, and U.S. Pat. No. 5344742, respectively. Moreover, a methylol melamine, resol resin, the novolak resin by which epoxidation was carried out, a urea-resin, etc. have been conventionally used also about the cross linking agent. However, in the conventional resist, it had the inadequate spreading homogeneity on a substrate, and the problem of defective generating at the time of development.

[0005]

[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is excellent in the spreading homogeneity in a substrate side, and is to offer the negative-resist constituent for an electron ray or X-rays which mitigated defective generating at the time of development.

[0006]

[Means for Solving the Problem] this invention person etc. resulted in a header and this invention that many above-mentioned purposes of this invention were attained by using a specific cross linking agent and a specific partially aromatic solvent depending on the type of a photosensitive constituent in the negative-mold chemistry multiplier system, as a result of inquiring wholeheartedly. That is, this invention is attained by the following configuration.

(1) The negative-resist constituent for an electron ray or X-rays characterized by containing following (A), (B), (C1), (D), and (E) at least.

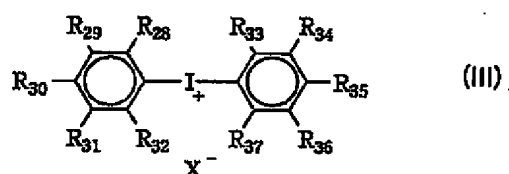
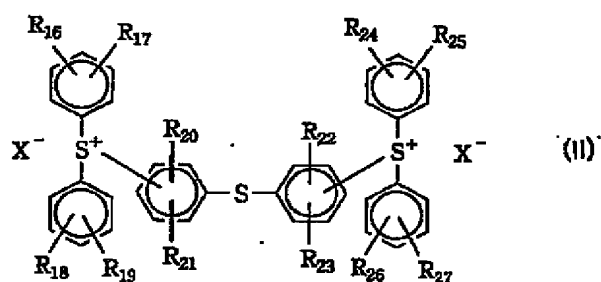
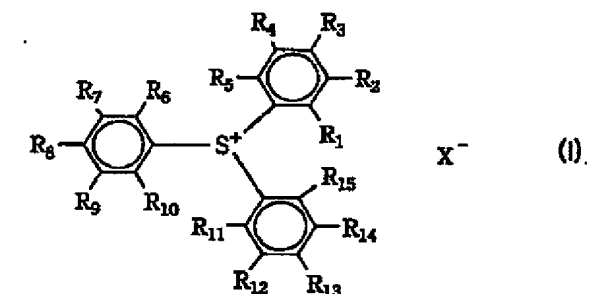
(A) It is the phenol derivative which contains 3-10 benzene ring atomic groups in the alkali fusibility (resin B) acid generator (C1) intramolecular. It has 2000 or less molecular weight, a hydroxymethyl group, and one or more alkoxy methyl groups in intramolecular, respectively. Among the solvents of a (cross linking agent D) organic base nature (compound E) following a group in which crosslinking reaction is shown according to the operation of an acid which has combined them with one of benzene ring atomic groups at least, at least one sort, partially aromatic solvent a group: containing at least one sort in the solvent of following b group, and the solvent of following c group -- propylene glycol monoalkyl ether carboxylate b group: -- propylene glycol monoalkyl ether -- Alkoxy propionic-acid alkyl [ lactic-acid alkyl and ] c group: The negative-resist constituent for an electron ray or X-rays given in gamma-butyrolactone, ethylene carbonate, and propylene carbonate (2) (1) further characterized by the following (C2) and/or (C3) containing.

It is the phenol derivative which contains 3-10 benzene ring atomic groups in intramolecular. (C2) It has two or more alkoxy methyl groups in intramolecular excluding 2000 or less molecular weight and a hydroxymethyl group. It is the phenol derivative which contains 3-10 benzene ring groups in the cross linking agent (C3)

intramolecular which has combined them with one of benzene ring groups at least, and which shows crosslinking reaction according to an operation of an acid. It has two or more hydroxymethyl groups in intramolecular excluding 2000 or less molecular weight and an alkoxy methyl group. The cross linking agent (3) which shows crosslinking reaction according to an operation of an acid and the (B) acid generator which have combined them with one of benzene ring atomic groups at least The negative-resist constituent for an electron ray or X-rays given in (1) characterized by being the compound shown by either the following general formula (I) or - (III), or (2).

[0007]

[Formula 2]



[0008] In [general formula (I) - (III), R1-R37 express respectively a hydrogen atom, an alkyl group, an alkoxy group, hydroxyl, a halogen atom, or the radical that can be shown by -S-R38 independently. R38 expresses an alkyl group or an aryl group. In the case of R1-R15, through the element which is chosen from them and which joins together and suits at the direct end mutually, or is chosen from oxygen, sulfur, and nitrogen, it joins together, and there are two or more, and they may form the ring structure. In R16-R27, the ring structure may be formed similarly. In R28-R37, the ring structure may be formed similarly. X- shows the anion of an organic sulfonic acid. ]

(4) The negative-resist constituent for an electron ray or X-rays given in (3) characterized by permuting by the organic radical by which X- was the anion of the organic sulfonic acid chosen from benzenesulfonic acid, the naphthalene sulfonic acid, or the anthracene sulfonic acid in the acid generator of a general formula (I) - (III), and a part or all of a hydrogen atom is permuted by the fluorine atom, or a part or all of a hydrogen atom

was permuted by the fluorine atom.

[0009] The following \*\* and \*\* are mentioned as a mode of the negative-resist constituent of this invention.

\*\* It is the negative resist containing alkali fusibility resin, an acid generator, a cross linking agent, an organic base nature compound, and an organic solvent, and is the cross linking agent which the cross linking agent became with the phenol derivative which contains 3-10 benzene ring atomic groups in intramolecular, molecular weight had 2000 or less, a hydroxymethyl group, and one or more alkoxy methyl groups in intramolecular, respectively, has combined them with one of benzene ring atomic groups at least, and constructs a bridge with an acid.

\*\* It is the negative resist containing alkali fusibility resin, the acid generator shown by the general formula (I) - the general formula (III), a cross linking agent, an organic base nature compound, and an organic solvent, and is the cross linking agent which the cross linking agent became with the phenol derivative which contains 3-10 benzene ring atomic groups in intramolecular, molecular weight had 2000 or less, a hydroxymethyl group, and one or more alkoxy methyl groups in intramolecular, respectively, has combined them with one of benzene ring atomic groups at least, and constructs a bridge with an acid.

In this invention, the mode of \*\* is desirable at the point that the effectiveness of this invention becomes fitness further among the modes of the above-mentioned \*\* and \*\*.

[0010]

[Embodiment of the Invention] Hereafter, the compound used for this invention is explained.

(A) Use alkali fusibility resin with an acid generator etc. in alkali fusibility resin this invention used by this invention. the alkali fusibility resin used with an acid generator etc. -- water -- it is insoluble and is resin meltable in an alkali water solution. As alkali fusibility resin used with an acid generator etc. For example, novolak resin, hydrogenation novolak resin, acetone-pyrogallol resin, Polly o-hydroxystyrene, Polly m-hydroxystyrene, Polly p-hydroxystyrene, Hydrogenation polyhydroxy styrene, a halogen, or alkylation polyhydroxy styrene, A hydroxystyrene-N-permutation maleimide copolymer, o/p-, and a m/p-hydroxystyrene copolymer, the part to the hydroxyl group of polyhydroxy styrene -- O-alkylation object for example, 5-30-mol % O-methylation object and O-(1-methoxy) ethylation object -- O-(1-ethoxy) ethylation object, an O-2-tetrahydropyranyl ghost, O-acylation objects, such as O-(t-butoxycarbonyl) methylation object For example, (5 - 30-mol % o-acetylation object, O-(t-butoxy) carbonylation object), etc., Although a styrene maleic anhydride copolymer, a styrene-hydroxystyrene copolymer, an alpha-methyl-styrene-hydroxystyrene copolymer, carboxyl group content methacrylic system resin, and its derivative can be mentioned, it is not limited to these. alkali fusibility resin especially desirable also in the above-mentioned alkali fusibility resin -- a part of novolak resin and Polly o-hydroxystyrene, Polly m-hydroxystyrene, Polly p-hydroxystyrene and these copolymer, alkylation polyhydroxy styrene, and polyhydroxy styrene -- they are O-alkylation or O-acylation object, a styrene-hydroxystyrene copolymer, and an alpha-methyl-styrene-hydroxystyrene copolymer.

[0011] The above-mentioned novolak resin is obtained by carrying out addition condensation to aldehydes under existence of an acid catalyst by using a predetermined monomer as a principal component. As a predetermined monomer, a phenol, m-cresol, p-cresol, Cresol, such as o-cresol, 2, 5-xyleneol, 3,5-xyleneol, Xyleneols, such as 3, 4-xyleneol, 2, and 3-xyleneol m-ethylphenol, p-ethylphenol, o-ethylphenol, Alkylphenols, such as p-t-butylphenol, p-octyl phenol, 2 and 3, and a 5-trimethyl phenol p-methoxy phenol, m-methoxy

phenol, 3, 5-dimethoxy phenol, 2-methoxy-4-methyl phenol, an m-ethoxy phenol, a p-ethoxy phenol, An m-propoxy phenol, a p-propoxy phenol, an m-butoxy phenol, Bis-alkylphenols, such as alkoxy phenols, such as a p-butoxy phenol, and a 2-methyl-4-isopropyl phenol independent in hydroxy aroma compounds, such as m-chlorophenol, p-chlorophenol, o-chlorophenol, a dihydroxy biphenyl, bisphenol A, phenylphenol, resorcinol, and a naphthol, -- or, although two or more kinds can use it, mixing It is not limited to these.

[0012] As aldehydes, for example Formaldehyde, a paraformaldehyde, An acetaldehyde, propionaldehyde, a benzaldehyde, phenylacetaldehyde, alpha-phenylpropyl aldehyde, beta-phenylpropyl aldehyde, Ortho hydroxybenzaldehyde, an m-hydroxy benzaldehyde, A p-hydroxy benzaldehyde, o-chlorobenzaldehyde, m-chlorobenzaldehyde, p-chlorobenzaldehyde, o-nitro benzaldehyde, m-nitro benzaldehyde, p-nitro benzaldehyde, o-methyl benzaldehyde, m-methyl benzaldehyde, Although p-methyl benzaldehyde, p-ethyl benzaldehyde, a p-n-butyl benzaldehyde, a furfural, chloroacetaldehyde, and these acetal objects, for example, a chloroacetaldehyde diethyl acetal etc., can be used In these, it is desirable to use formaldehyde. These aldehydes are independent, or they are combined two or more kinds and used. As an acid catalyst, a hydrochloric acid, a sulfuric acid, a formic acid, an acetic acid, oxalic acid, etc. can be used.

[0013] In this way, as for the weight average molecular weight of the obtained novolak resin, it is desirable that it is the range of 1,000-30,000. Less than by 1,000, if the film decrease after the development of the exposure section is large and exceeds 30,000, a development rate will become small. The range especially of a suitable thing is 2,000-20,000. moreover, the weight average molecular weight of said polyhydroxy styrene other than novolak resin and its derivative, and a copolymer -- 2000 or more -- desirable -- 2000-30000 -- it is 2000-20000 more preferably. Here, weight average molecular weight has the polystyrene reduced property of gel permeation chromatography, and is defined. The alkali dissolution rate of alkali fusibility resin is measured by 0.261-N tetramethylammonium hydroxide (TMAH) (23 degrees C), and its thing 20A [ /second ] or more is desirable. It is a thing 200A [ /second ] or more especially preferably. These alkali fusibility resin in this invention may be used independently, and two or more kinds may use it, mixing. The amount of the alkali fusibility resin used is usually 50 - 80 % of the weight preferably 30 to 90% of the weight on the basis of the total weight (except for a solvent) of a resist constituent.

[0014] (B) The acid generator used for acid generator this invention is a compound which generates an acid by the exposure of an electron ray or an X-ray. First, in this invention, the acid generator shown by said general formula (I) - general formula (III) which are a desirable acid generator is explained. even when R1-R37 in a general formula (I) - a general formula (III) are the same -- differing -- \*\*\*\* -- each -- they are an alkyl group, an alkoxy group, hydroxyl, a halogen atom, or the radical that can be shown by -S-R38 independently. A straight chain-like is sufficient as the alkyl group which R1-R37 express, the letter of branching is sufficient as it, and annular is sufficient as it. As the shape of a straight chain, and a letter alkyl group of branching, the alkyl group of 1-4 carbon numbers, such as a methyl group, an ethyl group, a propyl group, n-butyl, sec-butyl, and t-butyl, can be mentioned, for example. As an annular alkyl group, alkyl groups of 3-8 carbon numbers, such as a cyclo propyl group, a cyclopentyl group, and a cyclohexyl radical, can be mentioned, for example. A straight chain-like is sufficient as the alkoxy group which R1-R37 express, the letter of branching is sufficient as it, and an annular alkoxy group is sufficient as it. As the shape of a straight chain, and a letter alkoxy group of branching, the thing of 1-8 carbon numbers, for example, a methoxy group, an ethoxy radical, a hydroxy ethoxy radical, a propoxy group, an n-butoxy radical, an iso butoxy radical, a

sec-butoxy radical, a t-butoxy radical, an octyloxy radical, etc. can be mentioned, for example. As an annular alkoxy group, a cyclopenthyloxy radical and a cyclohexyloxy radical are mentioned, for example.

[0015] As a halogen atom which R1-R37 express, a fluorine atom, a chlorine atom, a bromine atom, and iodine atom can be mentioned. R38 in -S-R38 which R1-R37 express is an alkyl group or an aryl group. All in the alkyl group already enumerated as range of the alkyl group which R38 expresses as an alkyl group which R1-R37 express, for example can be mentioned. The aryl group which R38 expresses can mention the aryl group of 6-14 carbon numbers, such as a phenyl group, a tolyl group, a methoxyphenyl radical, and a naphthyl group. Each aryl group could combine the substituent with a part of radical further, the carbon number may be increased, and it is not necessary to have the substituent below the alkyl group that R1-R38 express. Furthermore, as a substituent which may be combined, the alkoxy group of 1-4 carbon numbers, the aryl group of 6-10 carbon numbers, and the alkenyl radical of 2-6 carbon numbers can be mentioned, and a cyano group, a hydroxy group, a carboxy group, an alkoxy carbonyl group, a nitro group, etc. can be mentioned preferably. In addition, a halogen atom is sufficient. For example, a fluorine atom, a chlorine atom, and iodine atom can be mentioned.

[0016] Two or more of them may join together, and the radical shown by R1-R15 in a general formula (I) may form the ring. The end of the radical shown by R1-R15 may couple directly and form a ring. Through one sort or two sorts or more of elements chosen from carbon, oxygen, sulfur, and nitrogen, it may connect indirectly, and may suit, and the ring may be formed. The structure same as a ring structure which two or more of R1-R15 combine and form as the ring structure looked at by a furan ring, a dihydrofuran ring, a pyran ring, a trihydro pyran ring, a thiophene ring, the pyrrole ring, etc. can be mentioned. It can say that the same is said of R16-R27 in a general formula (II). Two or more may join together directly or indirectly, and they may form the ring. The same is said of R28-R37 in a general formula (III). In a general formula (I) - (III), X- shows the anion of an organic sulfonic acid. As for an organic sulfonic acid, it is desirable to permute by the organic radical by which it was the organic sulfonic acid chosen from benzenesulfonic acid, the naphthalene sulfonic acid, or the anthracene sulfonic acid, and a part or all of a hydrogen atom is permuted by the fluorine atom, or a part or all of a hydrogen atom was permuted by the fluorine atom. As an organic radical permuted by the fluorine atom, an alkyl group, an alkoxyl group, an acyl group, an acyloxy radical, a sulfonyl group, a sulfonyloxy radical, a sulfonylamino radical, an aryl group, an aralkyl radical, an alkoxy carbonyl group, etc. can be mentioned, for example.

[0017] The alkyl group permuted by the fluorine atom At least one fluorine atom, The shape of a straight chain of carbon numbers 1-12 preferably permuted by 25 or less fluorine atoms, The letter of branching or an annular alkyl group is desirable. For example, a TORIFURORO methyl group, The Pentough Rollo ethyl group, 2 and 2, 2-TORIFURORO ethyl group, a heptaphloropropyl radical, a hepta-FURORO isopropyl group, perphloro butyl, a perphloro octyl radical, the perphloro dodecyl, a perphloro cyclohexyl radical, etc. can be mentioned. Especially, the perphloroalkyl group of the carbon numbers 1-4 altogether permuted with the fluorine is desirable. The alkoxyl group permuted by the fluorine atom has at least one fluorine atom and the desirable carbon number preferably permuted by 25 or less fluorine atoms, for example, the shape of a straight chain of 1-12, the letter of branching, or an annular alkoxyl group can mention a TORIFURORO methoxy group, a pen TAFURORO ethoxy radical, a hepta-FURORO isopropoxy radical, a perphloro butoxy radical, a perphloro octyloxy radical, a perphloro dodecyloxy radical, a perphloro cyclohexyloxy radical, etc.

Especially, the perphloro alkoxy group of the carbon numbers 1–4 altogether permuted with the fluorine is desirable. The acyl group permuted by the fluorine atom has that desirable by which carbon numbers are 2–12, and are permuted by 1–23 fluorine atoms. Specifically, the Tori Flo Roar cetyl group, the Flo Roar cetyl group, a pen TAFURORO propionyl radical, the Pentough Rollo benzoyl, etc. can be mentioned.

[0018] The acyloxy radical permuted by the fluorine atom has that desirable by which carbon numbers are 2–12, and are permuted by 1–23 fluorine atoms. Specifically, a TORIFURORO acetoxy radical, a FURORO acetoxy radical, a pen TAFURORO propionyloxy radical, a pen TAFURORO benzoyloxy radical, etc. can be mentioned. That by which carbon numbers are 1–12, and are permuted by 1–25 fluorine atoms as a sulfonyl group permuted by the fluorine atom is desirable. Specifically, a truffe ROROME tongue sulfonyl group, the Pentough ROROE tongue sulfonyl group, a perphloro butane sulfonyl group, a perphloro octane sulfonyl group, a pen TAFURORO benzenesulphonyl radical, 4-trifluoromethylbenzene sulfonyl group, etc. can be mentioned. That by which the carbon number is permuted as a sulfonyloxy radical permuted by the fluorine atom by the fluorine atom they are [ atom ] 1–12, and 1–25 pieces is desirable. Specifically, truffe ROROME tongue sulfonyloxy, a perphloro butane sulfonyloxy radical, 4-trifluoromethylbenzene sulfonyloxy radical, etc. can be mentioned. As a sulfonylamino radical permuted by the fluorine atom, carbon numbers are 1–12 and what is permuted by 1–25 fluorine atoms is desirable. Specifically, a truffe ROROME tongue sulfonylamino radical, a perphloro butane sulfonylamino radical, a perphloro octane sulfonylamino radical, a pen TAFURORO benzenesulphonyl amino radical, etc. can be mentioned.

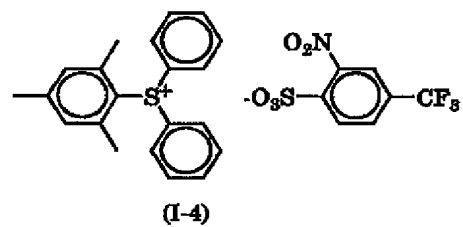
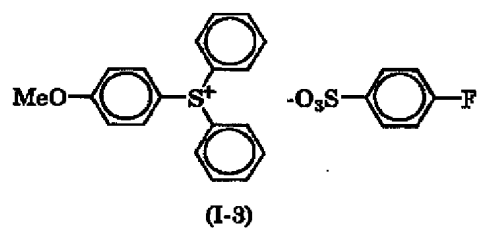
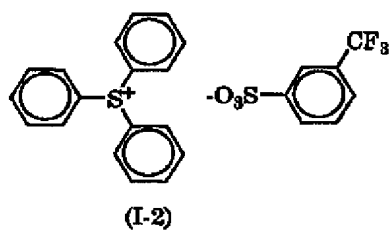
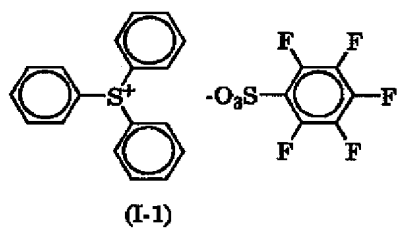
[0019] That by which carbon numbers are 6–14, and are permuted by 1–9 fluorine atoms as an aryl group permuted by the fluorine atom is desirable. Specifically, Pentough Rollo phenyl group, 4-truffe ROROME chill phenyl group, hepta-FURORO naphthyl group, nona FURORO anthranil, 4-FURORO phenyl group, 2, and 4-JIFURORO phenyl group etc. can be mentioned. That by which carbon numbers are 7–10, and are permuted by 1–15 fluorine atoms as an aralkyl radical permuted by the fluorine atom is desirable. Specifically, a pen TAFURORO phenylmethyl radical, a pen TAFURORO phenylethyl radical, perphloro benzyl, a perphloro phenethyl radical, etc. can be mentioned. That by which carbon numbers are 2–13, and are permuted by 1–25 fluorine atoms as an alkoxy carbonyl group permuted by the fluorine atom is desirable. Specifically, a TORIFURORO methoxycarbonyl group, a pen TAFURORO ethoxycarbonyl radical, a pen TAFURORO phenoxy carbonyl group, a perphloro butoxycarbonyl radical, a perphloro octyloxy carbonyl group, etc. can be mentioned.

[0020] Most desirable X<sup>-</sup> in such an anion is a fluorine permutation benzenesulfonic acid anion, and especially its pentafluoro benzenesulfonic acid anion is desirable especially. Moreover, the benzenesulfonic acid which has the above-mentioned fluorine-containing substituent, a naphthalene sulfonic acid, or an anthracene sulfonic acid may be further permuted by the shape of a straight chain, the letter of branching or an annular alkoxy group, an acyl group, an acyloxy radical, a sulfonyl group, a sulfonyloxy radical, a sulfonylamino radical, an aryl group, an aralkyl radical, the alkoxy carbonyl group (these carbon number range is the same as that of the aforementioned thing), the halogen (except for a fluorine), the hydroxyl group, a nitro group, etc. Although the example of a compound expressed with these general formulas (I) – (III) below is shown, it is not limited to this.

[0021]

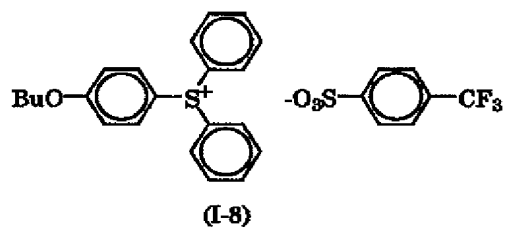
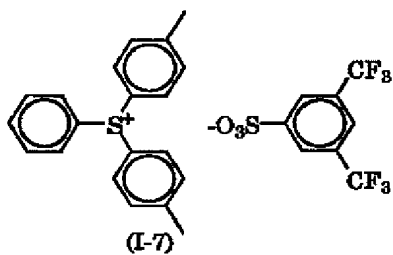
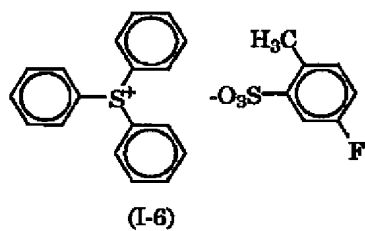
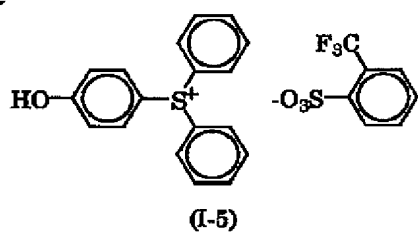
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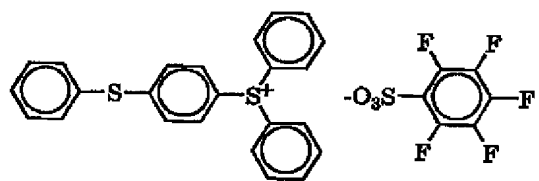
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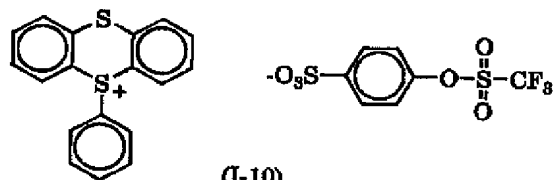


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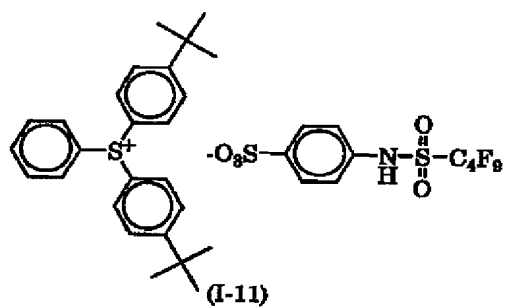
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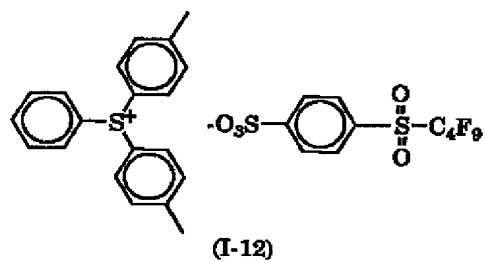
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(I-10)



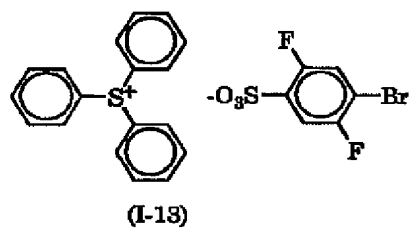
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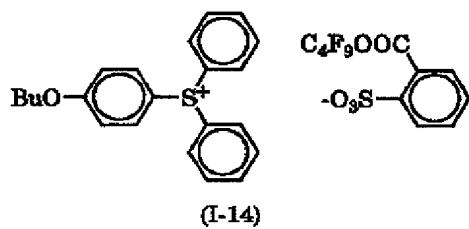
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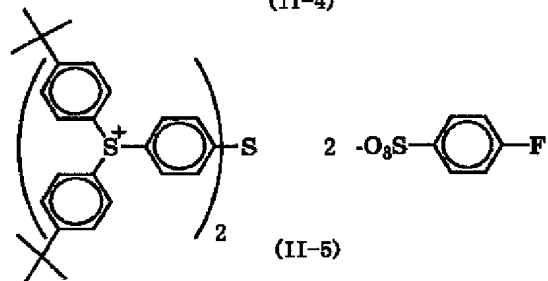
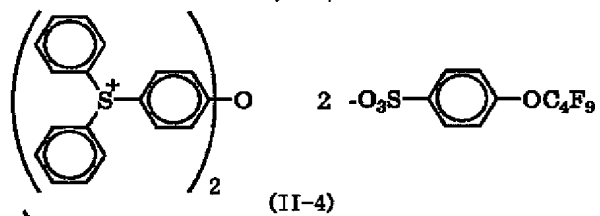
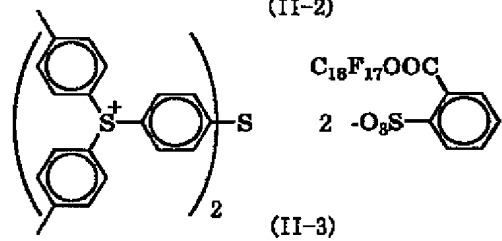
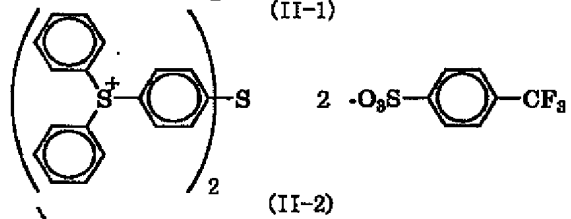
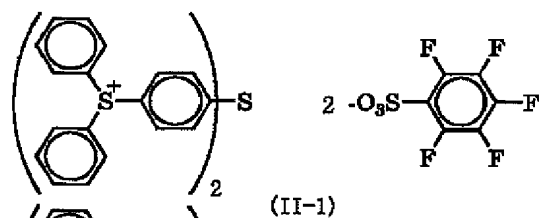
(I-13)



(I-14)

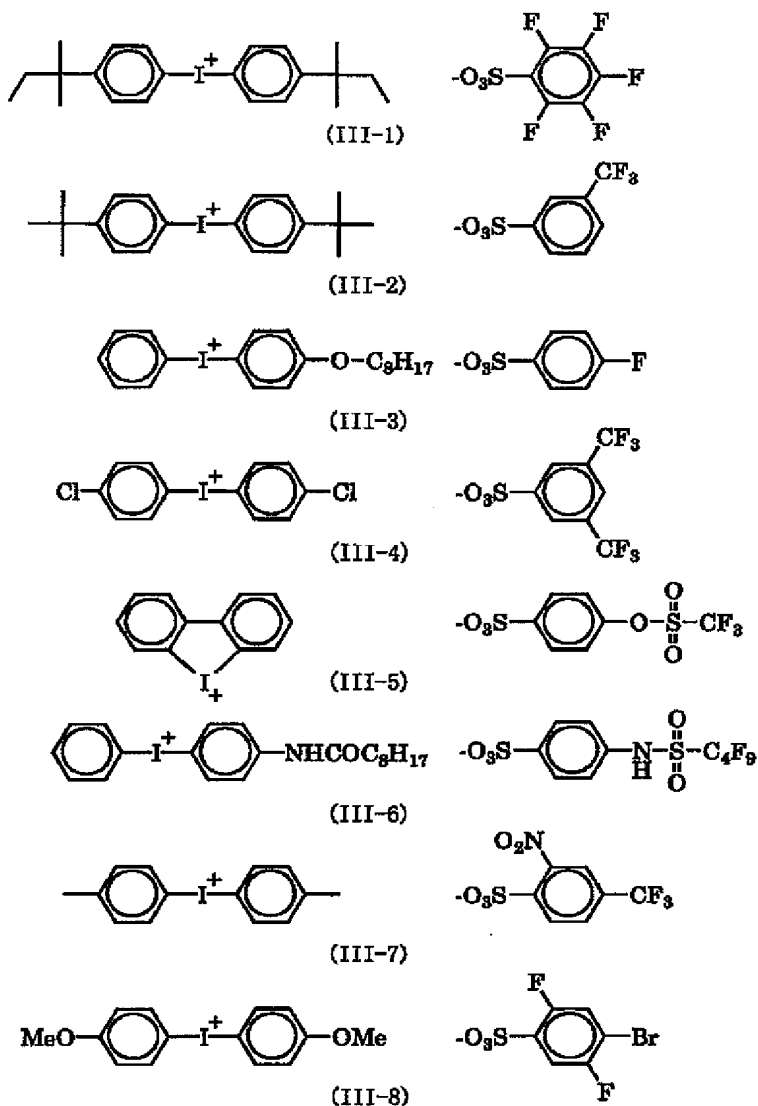
[0025]

[Formula 7]



[0026]

[Formula 8]



[0027] The compound of a general formula (I) and a general formula (II) is compoundable by the following approaches. For example, an aryl Grignard reagent and phenyl sulfoxides, such as aryl magnesium bromide, are made to react, and salt exchange of the obtained triarylsulfonium halide is carried out with a corresponding sulfonic acid. There is also an option. For example, there are condensation and the approach of carrying out salt exchange using acid catalysts, such as methansulfonic acid / diphosphorus pentoxide, or chlorination aluminum, about a phenyl sulfoxide and a corresponding aromatic compound. Moreover, a diaryl iodonium salt and a diaryl sulfide are compoundable by condensation, the approach of carrying out salt exchange, etc. using catalysts, such as copper acetate. The phenyl sulfoxide may be making the substituent permute by the benzene ring by any above-mentioned approach, and there may not be such a substituent. The compound of a general formula (III) is compoundable by making an aromatic compound react using a periodate. 0.1 - 20 % of the weight is suitable for the content of the acid generator used by this invention to the solid content of all negative-resist constituents, and it is 1 - 7 % of the weight still more preferably 0.5 to 10% of the weight preferably. When a compound which is expressed with either a general formula (I) or - the general formulas (III) is included as an acid generator, 0.1 - 20 % of the weight is suitable for the content to

the solid content of all negative-resist constituents, and it is 1 – 7 % of the weight still more preferably 0.5 to 10% of the weight preferably.

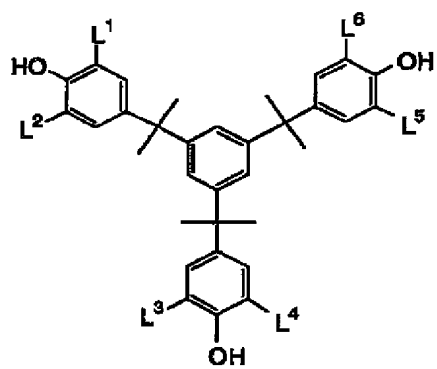
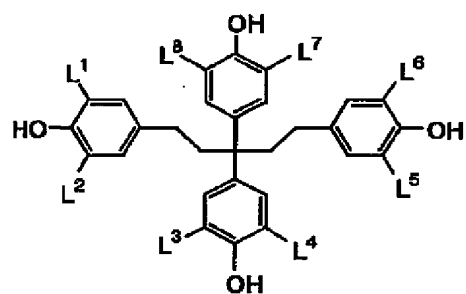
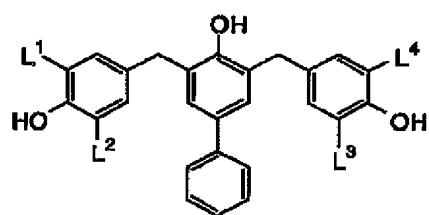
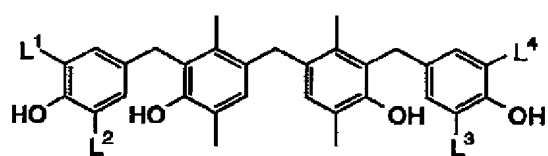
[0028] (Other acid generators) In this invention, other compounds which decompose by the exposure of electron rays other than the compound expressed with the above-mentioned general formula (I) – a general formula (III) or an X-ray, and generate an acid can also be used. Moreover, other compounds which decompose by the exposure of the compound expressed with a general formula (I) – a general formula (III), an electron ray, or an X-ray, and generate an acid may be used together. In this case, the ratio with other compounds which decompose by the exposure of the compound expressed with a general formula (I) – a general formula (III), an electron ray, or an X-ray, and generate an acid — a mole ratio — 100 / 0 – 20/80 — desirable — 90 / 10 – 40/60 — it is 80 / 20 – 50/50 still more preferably. The compounds which decompose as such other acid generators by the exposure of the electron ray or X-ray currently used for the photoinitiator of optical cationic polymerization, the photoinitiator of an optical radical polymerization, the optical decolorizing agent of coloring matter, optical alterant, or a micro resist, and generate an acid, and those mixture can be used choosing them suitably. For example, the compound and disulfon compound which are represented by onium salt, such as diazonium salt, phosphonium salt, iodonium salt, sulfonium salt, a seleno NIUMU salt, and arsonium salt, an organic halogenated compound, an organic metal / organic halogenide, the acid generator that has o-nitrobenzyl mold protective group, imino sulfonate, etc. and which decompose and generate a sulfonic acid can be mentioned.

[0029] Moreover, the compound of a publication can be used for the radical which generates an acid by the exposure of an electron ray or an X-ray or the compound which introduced the compound into the principal chain or side chain of a polymer, for example, JP,63-26653,A, JP,55-164824,A, JP,62-69263,A, JP,63-146038,A, JP,63-163452,A, JP,62-153853,A, JP,63-146029,A, etc. Furthermore, the compound which generates the acid of a publication can also be used for U.S. Pat. No. 3,779,778, the Europe patent No. 126,712, etc.

[0030] (C) In cross linking agent this invention used by this invention as a compound (the following — suitably — an acid cross linking agent — or a cross linking agent only being called) which constructs a bridge with an acid Molecular weight 2000 (it is desirable, 1200 or less and a minimum are desirable, and it is 300) or less It has a hydroxymethyl group and one or more alkoxy methyl groups each at least including the 3–10 benzene rings (preferably 3–5 pieces) in intramolecular. The phenol derivative of them (C1) (cross linking agent) which is made to concentrate on one of the benzene rings at least, or distributes, and it comes to join together is used for the hydroxymethyl group and an alkoxy methyl group. As an alkoxy methyl group combined with the benzene ring, the thing of six or less carbon numbers is desirable. Specifically, a methoxymethyl radical, an ethoxy methyl group, an n-propoxy methyl group, an i-propoxy methyl group, an n-butoxy methyl group, an i-butoxy methyl group, a sec-butoxy methyl group, and a t-butoxy methyl group are desirable. Furthermore, the alkoxy group by which the alkoxy permutation was carried out is also desirable like a 2-methoxyethoxy radical and a 2-methoxy-1-propoxy group. A desirable thing is especially listed to below among these phenol derivatives.

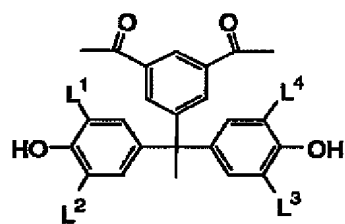
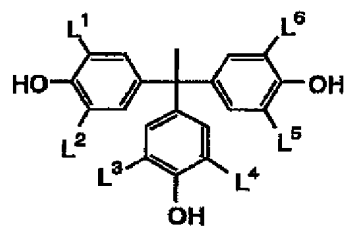
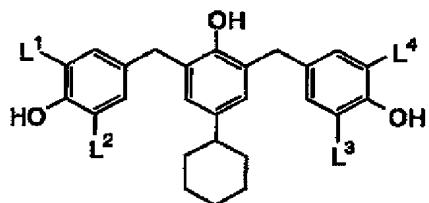
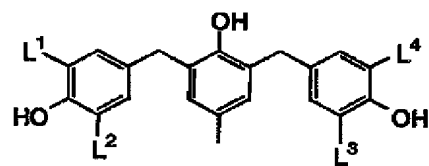
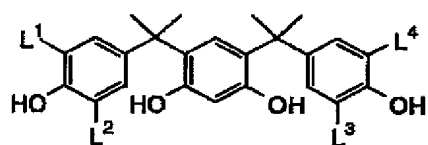
[0031]

[Formula 9]



[0032]

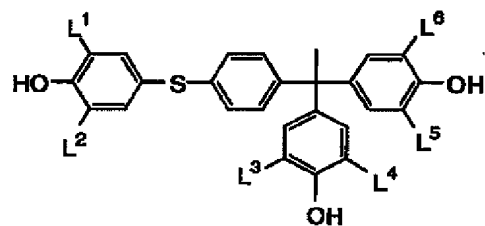
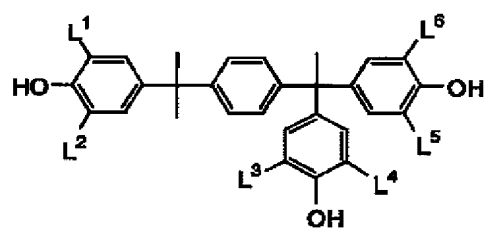
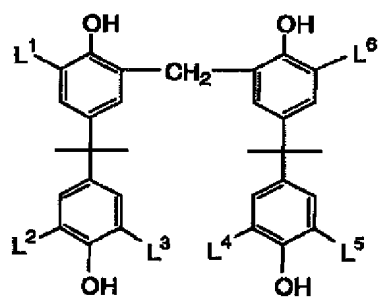
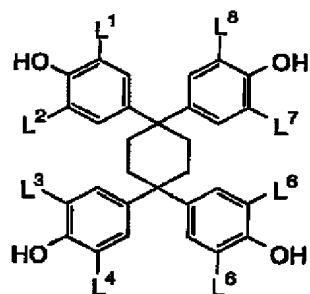
[Formula 10]



[0033]

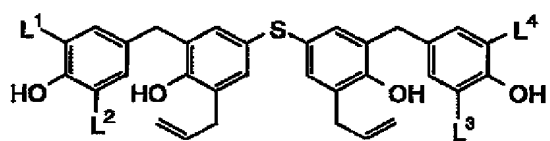
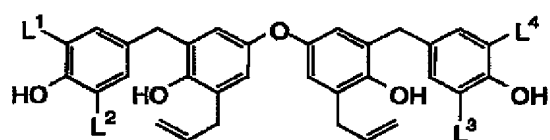
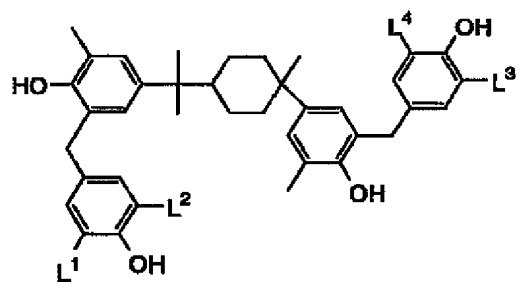
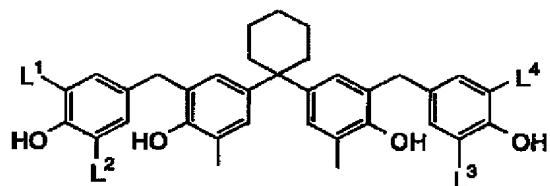
[Formula 11]





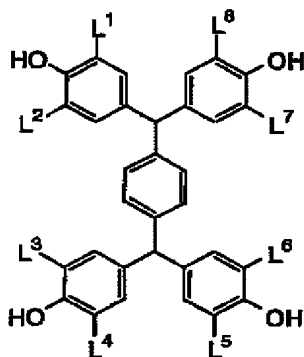
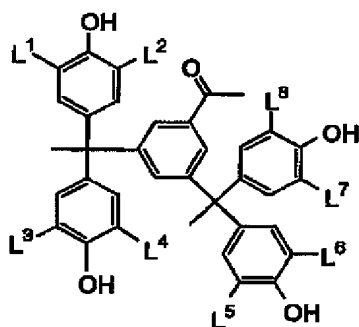
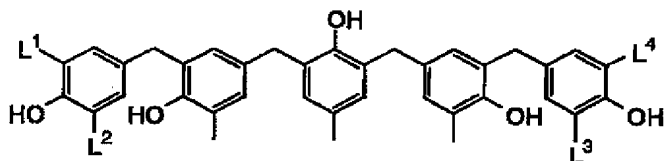
[0034]

[Formula 12]



[0035]

[Formula 13]



[0036] (L1–L8 show a hydroxymethyl group, a methoxymethyl radical, or an ethoxy methyl group among a formula.) However, each compound has at least one piece, a methoxymethyl radical, or at least one ethoxy methyl group for a hydroxymethyl group.

The cross linking agent of this invention is compounded by carrying out partial alkoxy methylation of it by making into an intermediate product the phenol derivative which has a hydroxymethyl group. The phenol derivative which has a hydroxymethyl group can be obtained by making the phenolic compound (compound L1–whose L8 are the hydrogen atoms in the above–mentioned formula) and formaldehyde which do not have a corresponding hydroxymethyl group react under a base catalyst. Under the present circumstances, in order to prevent resinification and gelation, it is desirable to perform reaction temperature below 60 degrees C. Specifically, it is compoundable by the approach indicated by JP,6–282067,A, JP,7–64285,A, etc. Partial alkoxy methylation can be acquired by making the phenol derivative and alcohol which have a corresponding hydroxymethyl group react under an acid catalyst. Under the present circumstances, in order to prevent resinification and gelation, it is desirable to perform reaction temperature below 100 degrees C. Specifically, it is compoundable by the approach indicated by the Europe patent EP632003A1 grade. As a conversion rate from the methylol radical of an intermediate product to an alkoxy methyl group, it is 50 – 95% (above NMR measured value) still more preferably 30 to 96% preferably 20 to 98% as mixture. Moreover, the content of the compound with which all the methylol radicals were completely permuted by the alkoxy methyl group is 60 – 90% (above HPLC measured value) still more preferably 50 to 93% preferably 20 to 96%. Such a phenol

derivative that has respectively a hydroxymethyl group and one or more alkoxy methyl groups, and is made to concentrate on one of the benzene rings, or distributes, and it comes to join together may be used independently, and may be used combining two or more sorts. The above-mentioned cross linking agent (C1) is usually preferably used with 5 – 50% of the weight of an addition three to 70% of the weight among [ all ] resist constituent solid content. When there is an inclination for a remaining rate of membrane to fall that an addition is less than 3 % of the weight and 70 % of the weight is exceeded, resolving power declines and there is an inclination which is not still not much more desirable in respect of the stability at the time of preservation of resist liquid.

[0037] Moreover, the negative-resist constituent of this invention is a phenol derivative which contains 3–10 benzene ring atomic groups (preferably 3–5 pieces) in intramolecular further. 2000 or less (it is desirable, 1200 or less and a minimum are desirable, and it is 300) molecular weight, It has two or more alkoxy methyl groups in intramolecular excluding a hydroxymethyl group. The cross linking agent which shows crosslinking reaction according to the operation of an acid which has combined them with one of benzene ring atomic groups at least (C2), And it is the phenol derivative which contains 3–10 benzene ring atomic groups (preferably 3–5 pieces) in intramolecular. 2000 or less (it is desirable, 1200 or less and a minimum are desirable, and it is 300) molecular weight, It has two or more hydroxymethyl groups in intramolecular excluding an alkoxy methyl group, and the cross linking agent which shows crosslinking reaction according to the operation of an acid which has combined them with one of benzene ring atomic groups at least (C3) may be included. (C1) the case where a cross linking agent is used together in addition to (C2) (C3) a cross linking agent -- as the total quantity of -- (C1) (C3) cross linking agent -- all the inside of resist constituent solid content -- it is 7 – 30 % of the weight still more preferably five to 50% of the weight preferably three to 60% of the weight. (C1) – (C3) -- 51 – 97 % of the weight is desirable still more desirable to the total quantity of a cross linking agent, the content of a cross linking agent (C2) is 60 – 95 % of the weight, 2 – 40 % of the weight is desirable still more desirable, and the content of a cross linking agent (C3) is 3 – 20 % of the weight.

[0038] In addition to the above-mentioned phenol derivative, in this invention, other following cross linking agents (i) and (ii) may be used together. the ratio of the total quantity of the above-mentioned -- (C1) (C3) cross linking agent, and other cross linking agents which can be used together with this -- a mole ratio -- 100 / 0 – 20/80 -- desirable -- 90 / 10 – 40/60 -- it is 80 / 20 – 50/50 still more preferably.

(i) Compound (ii) which has N-hydroxymethyl group, an N-alkoxy methyl group, or N-acyloxy methyl group an epoxy compound -- the cross linking agent of these is explained below at a detail.

(i) As a compound which has N-hydroxymethyl group, an N-alkoxy methyl group, or N-acyloxy methyl group, the benzoguanamine-formaldehyde condensate indicated by the urea-formaldehyde condensate, the alkoxy substituted compound indicated at EP-A No. 0,212,482 is mentioned to the monomer and oligomer-melamine-formaldehyde condensate list indicated by the Europe patent public presentation (it is hereafter indicated as "EP-A") No. 0,133,216, the West German patent No. 3,634,671, and 3,711,264. Furthermore, as a desirable example, the melamine-formaldehyde derivative which has at least two isolation N-hydroxymethyl groups, an N-alkoxy methyl group, or N-acyloxy methyl group is mentioned, for example, and especially an N-alkoxy methyl derivative is desirable especially.

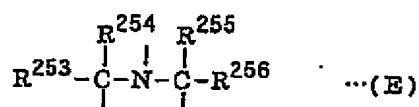
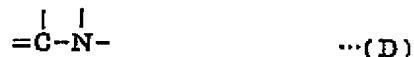
[0039] (ii) As an epoxy compound, the epoxy compound of the shape of the monomer and dimer containing one or more epoxy groups, oligomer, and a polymer can be mentioned. For example, the resultant of

bisphenol A and epichlorohydrin, the resultant of low-molecular-weight phenol-formaldehyde resin and epichlorohydrin, etc. are mentioned. In addition, the epoxy resin which is indicated by a U.S. Pat. No. 4,026,705 official report and the British patent No. 1,539,192 official report, and is used for them can be mentioned. (C1) the case where cross linking agents other than a cross linking agent are used together — a cross linking agent (C1) — including — the total amount of a cross linking agent — all the inside of resist constituent solid content — it is preferably used at 7 – 40 % of the weight still more preferably five to 60% of the weight three to 70% of the weight.

[0040] (D) The desirable organic base nature compound which can be used by organic base nature compound this invention is a compound with basicity stronger than a phenol. A nitrogen-containing basicity compound is desirable especially. As desirable chemical environment, the structure of following type (A) – (E) can be mentioned.

[0041]

[Formula 14]



[0042] Here, it is R250 and R251. And R252 It may be the same, or you may differ and the permutation of a hydrogen atom, the alkyl group of 1–6 carbon numbers, the amino alkyl group of 1–6 carbon numbers, the hydroxyalkyl radical of 1–6 carbon numbers, or 6–20 carbon numbers or an unsubstituted aryl group is expressed, it may join together mutually and R251 and R252 may form a ring here. R253, R254, and R255 And R256 It may be the same, or you may differ and the alkyl group of 1–6 carbon numbers is expressed. Furthermore, a desirable compound is a nitrogen-containing basicity compound which has two or more nitrogen atoms of different chemical environment in a monad, and is a compound which has especially a compound or alkylamino radical including both ring structures containing the amino group and nitrogen atom which are not permuted [ a permutation or ] preferably.

[0043] As a desirable example, the aminopyridine which is not permuted [ the guanidine which is not permuted / a permutation or / a permutation, or ], The amino pyrrolidine which is not permuted [ the amino alkyl pyridine which is not permuted / a permutation or / a permutation, or ], The pyrazole which is not permuted [ the indazole which is not permuted / a permutation or /, an imidazole, a permutation, or ], The pyrimidine which is not permuted [ the pyrazine which is not permuted / a permutation or /, a permutation,

or ], The amino alkyl morpholine which is not permuted [ the amino morpholine which is not permuted / the piperazine which is not permuted / the pyrazoline which is not permuted / the imidazoline which is not permuted / the pudding which is not permuted / a permutation or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or /, a permutation, or ] is mentioned. Desirable substituents are the amino group, an amino alkyl group, an alkylamino radical, an amino aryl group, an arylamino radical, an alkyl group, an alkoxy group, an acyl group, an acyloxy radical, an aryl group, an aryloxy group, a nitro group, a hydroxyl group, and a cyano group.

[0044] As a desirable compound, especially Guanidine, 1, and 1-dimethyl guanidine, 1, 1, 3, 3, - tetramethyl guanidine, an imidazole, 2-methylimidazole, 4-methyl imidazole, N-methyl imidazole, 2-phenylimidazole, 4, 5-diphenyl imidazole, 2 and 4, 5-triphenyl imidazole, 2-aminopyridine, 3-aminopyridine, 4-aminopyridine, 2-dimethylamino pyridine, 4-dimethylaminopyridine, 2-diethylamino pyridine, 2-(aminomethyl) pyridine, 2-amino-3-methylpyridine, 2-amino-4-methylpyridine, 2-amino-5-methylpyridine, 2-amino-6-methylpyridine, 3-aminoethyl pyridine, 4-aminoethyl pyridine, 3-amino pyrrolidine, A piperazine, N-(2-aminoethyl) piperazine, N-(2-aminoethyl) piperidine, 4-amino - 2, 2, 6, and 6-tetramethylpiperidine, 4-piperidino piperidine, A 2-imino piperidine, 1-(2-aminoethyl) pyrrolidine, a pyrazole, 3-amino-5-methyl pyrazole, 5 - Amino-3-methyl-1-p-tolyl pyrazole, Pyrazine, 2-(aminomethyl)-5-methyl pyrazine, a pyrimidine, Although 2, 4-diamino pyrimidine, 4, 6-dihydroxy pyrimidine, 2-pyrazoline, 3-pyrazoline, N-amino morpholine, N-(2-aminoethyl) morpholine, etc. are mentioned, it is not limited to this. These nitrogen-containing basicity compounds are independent, or are used together two or more sorts. As for the operating rate in the constituent of an acid generator and an organic base nature compound, it is desirable that it is a (acid generator) / (organic base nature compound) (mole ratio) = 2.5-300. This mole ratio may serve as low sensibility less than by 2.5, resolving power may decline, and if 300 is exceeded, \*\*\*\* of a resist pattern may become large by the passage of time to exposure afterbaking processing, and resolving power may also decline. a (acid generator) — / (organic base nature compound) (mole ratio) -- desirable -- 5.0-200 -- it is 7.0-150 still more preferably.

[0045] (E) The negative-resist constituent of partially aromatic solvent this invention contains the partially aromatic solvent which contains at least one sort (it is also called the solvent of b group) and/or gamma-butyrolactone, ethylene carbonate, and propylene carbonate (it is also called the solvent of c group) among propylene glycol monoalkyl ether carboxylate among at least one sort (it is also called the solvent of a group), propylene glycol monoalkyl ether and lactic-acid alkyl, and alkoxy propionic-acid alkyl as a (E) component. That is, as a (E) component, the combination of the solvent of a group and the solvent of b group, the combination of the solvent of a group and the solvent of c group, and the combination of the solvent of a group, the solvent of b group, and the solvent of c group are used.

[0046] As propylene glycol monoalkyl ether carboxylate, propylene-glycol-monomethyl-ether acetate, propylene-glycol-monomethyl-ether propionate, propylene glycol monoethyl ether acetate, and propylene glycol monoethyl ether propionate can be mentioned preferably.

[0047] As propylene glycol monoalkyl ether, propylene glycol monomethyl ether and the propylene glycol monoethyl ether can be mentioned preferably. As lactic-acid alkyl, methyl lactate and ethyl lactate can be mentioned preferably. As alkoxy propionic-acid alkyl, 3-ethoxy ethyl propionate, 3-methoxy ethyl propionate, 3-methoxy ethyl propionate, and 3-ethoxy methyl propionate can be mentioned preferably.

[0048] 90:10–15:85 are desirable, and are 80:20–20:80 more preferably, and the operating weight ratios (a:b) of the solvent of the above-mentioned a group and the solvent of b group are 70:30–25:75 still more preferably. 99.9:0.1–75:25 are desirable, and are 99:1–80:20 more preferably, and the operating weight ratios (a:c) of the solvent of the above-mentioned a group and the solvent of c group are 97:3–85:15 still more preferably.

[0049] When combining three sorts of these solvents, the operating weight ratio of the solvent of c group has 0.1 – 25 desirable % of the weight to all solvents, and is 3 – 17 % of the weight still more preferably one to 20% of the weight more preferably. In this invention, it is desirable to dissolve the solid content of the resist constituent containing each above-mentioned component in the above-mentioned partially aromatic solvent three to 25% of the weight as solid content concentration, it is 5 – 22 % of the weight more preferably, and is 7 – 20 % of the weight still more preferably.

[0050] As a desirable combination of the partially aromatic solvent in this invention

Propylene-glycol-monomethyl-ether acetate + propylene-glycol-monomethyl-ether  
propylene-glycol-monomethyl-ether acetate + ethyl lactate propylene-glycol-monomethyl-ether acetate  
+3-ethoxy ethyl propionate propylene glycol Monomethyl ether acetate + gamma-butyrolactone  
propylene-glycol-monomethyl-ether acetate + ethylene carbonate propylene-glycol-monomethyl-ether  
acetate + propylene carbonate propylene-glycol-monomethyl-ether acetate + PUROPIRE NGURU call  
monomethyl ether + gamma-butyrolactone propylene-glycol-monomethyl-ether acetate + ethyl lactate +  
gamma-butyrolactone propylene-glycol-monomethyl-ether acetate +3-ethoxy ethyl propionate +  
gamma-butyrolactone propylene GURIKO A RUMONO methyl ether acetate +  
propylene-glycol-monomethyl-ether + ethylene carbonate propylene-glycol-monomethyl-ether acetate +  
ethyl lactate + ethylene carbonate propylene-glycol-monomethyl-ether acetate +3-ethoxy propionic acid  
Ethyl + ethylene carbonate propylene-glycol-monomethyl-ether acetate +  
propylene-glycol-monomethyl-ether + propylene carbonate propylene glycol MONOMECHI It is RUETERU  
acetate + ethyl lactate + propylene carbonate propylene-glycol-monomethyl-ether acetate +3-ethoxy ethyl  
propionate + propylene carbonate.

[0051] As a combination of a desirable solvent, especially Propylene-glycol-monomethyl-ether acetate +  
propylene-glycol-monomethyl-ether + gamma-butyrolactone propylene-glycol-monomethyl-ether acetate  
+ ethyl lactate + gamma-butyrolactone propylene-glycol-monomethyl-ether acetate +3-ETOKI  
SHIPUROPION acid ethyl + gamma-butyrolactone propylene-glycol-monomethyl-ether acetate +  
propylene-glycol-monomethyl-ether + ethylene carbonate propylene-glycol-monomethyl-ether acetate +  
ethyl lactate + ethylene carbonate propylene GURIKO – RUMONO methyl ether acetate +3 – Ethoxy ethyl  
propionate + ethylene carbonate propylene-glycol-monomethyl-ether acetate +  
propylene-glycol-monomethyl-ether + propylene car BONE It is TOPUROPIRENGURIKORU monomethyl  
ether acetate + ethyl lactate + propylene carbonate propylene-glycol-monomethyl-ether acetate +3-ethoxy  
ethyl propionate + propylene carbonate.

[0052] The partially aromatic solvent used for the constituent of this invention may contain solvents other than the above-mentioned specific solvent in the range which does not bar the effectiveness of this invention. Generally such other solvents are 30 or less % of the weight of range to all solvents. As such a solvent, for example Ethylene glycol monomethyl ether, Ethylene glycol monoalkyl ether, such as ethylene

glycol monoethyl ether Ethylene glycol monoalkyl ether acetate, such as ethylene glycol monomethyl ether acetate and ethylene glycol monoethyl ether acetate Pyruvic-acid alkyl ester, such as 2-heptanone, methyl pyruvate, and pyruvic-acid ethyl N-methyl pyrrolidone, N,N-dimethylacetamide, dimethyl sulfoxide, Ethylene dichloride, a cyclohexanone, cyclopentanone, a methyl ethyl ketone, 2-methoxy ethyl acetate, toluene, ethyl acetate, N,N-dimethylformamide, a tetrahydrofuran, etc. can be mentioned.

[0053] (F) The negative-resist constituent of component this invention of others which are used for the constituent of this invention can be made to contain a color, a surfactant, etc. further if needed.

(F) -1 a color -- there are fat dye and basic dye as a suitable color. Specifically, oil yellow #101, oil yellow #103, oil pink #312, the oil green BG, oil blue BOS, oil blue #603, oil black BY, oil black BS, oil black T-505 (above the ORIENT chemical-industry incorporated company make), a crystal violet (CI42555), Methyl Violet (CI42535), rhodamine B (CI45170B), Malachite Green (CI42000), a methylene blue (CI52015), etc. can be mentioned.

[0054] (F) -2 A surfactant can also be added to the surfactants above-mentioned solvent. Specifically The polyoxyethylene lauryl ether, polyoxyethylene stearylether, Polyoxyethylene alkyl ether, such as the polyoxyethylene cetyl ether and the polyoxyethylene oleyl ether Polyoxyethylene alkyl aryl ether, such as the polyoxyethylene octyl phenol ether and the polyoxyethylene nonyl phenol ether Polyoxyethylene polyoxypropylene block copolymers Sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate, Sorbitan fatty acid esters, such as sorbitan monooleate, sorbitan trioleate, and sorbitan tristearate Polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, Polyoxyethylenesorbitan monostearate, polyoxyethylene sorbitan trioleate, The Nonion system surfactants, such as polyoxyethylene sorbitan fatty acid ester, such as polyoxyethylene sorbitan tristearate, EFUTOPPU EF301, EF303, and EF352 (new Akita formation Make), Megger fucks F171 and F173 (Dainippon Ink make) Fluorad FC430 and FC431 (Sumitomo 3M make), Fluorochemical surfactants, such as the Asahi guard AG710, Sir chlorofluocarbon S-382, and SC101, SC102, SC103, SC104, SC105, SC106 (Asahi Glass Co., Ltd. make), Organosiloxane polymer KP341 (Shin-Etsu Chemical Co., Ltd. make), an acrylic-acid system or methacrylic-acid system (\*\*) polymerization poly flow No.75, No.95 (product made from Kyoeisha Fats-and-oils Chemical industry), etc. can be mentioned. The loadings of these surfactants are usually below 1 weight section preferably below 2 weight sections per solid content 100 weight section in the constituent of this invention. You may add independently and these surfactants can also be added in some combination.

[0055] In addition, in the resist constituent of this invention, a fluorine system and/or a silicon system surfactant are contained preferably. It is desirable to contain either of the surfactants containing both a fluorochemical surfactant, a silicon system surfactant and a fluorine atom, and a silicon atom or two sorts or more in the resist constituent of this invention. As these surfactants, for example, JP,62-36663,A, JP,61-226746,A, JP,61-226745,A, JP,62-170950,A, JP,63-34540,A, JP,7-230165,A, JP,8-62834,A, JP,9-54432,A, JP,9-5988,A, a U.S. Pat. No. 5405720 number, said 5360692 numbers, said -- No. 5529881 -- said -- No. 5296330 -- said -- No. 5436098 -- said -- No. 5576143 -- said -- a surfactant No. 5294511 and given [ this ] in No. 5824451 can be mentioned, and the surfactant of the following marketing can also be used as it is. As a surfactant of marketing which can be used, for example, EFUTOPPU EF301 and EF303, (made in new Akita Chemicals), Fluorad 430 and FC 431 (Sumitomo 3M make), the megger fucks F171, F173,



F176, F189, and R08 (Dainippon Ink make), A fluorochemical surfactant or silicon system surfactants, such as Sir chlorofluocarbon S-382, SCs 101, 102, 103, 104, 105, and 106 (Asahi Glass Co., Ltd. make), and Troysol S-366 (made in Troy Chemical), can be mentioned. Moreover, polysiloxane polymer KP-341 (Shin-Etsu Chemical Co., Ltd. make) can be used as a silicon system surfactant. The loadings of a fluorine system and/or a silicon system surfactant are usually 0.01 % of the weight – 1 % of the weight preferably on the basis of the solid content in the constituent of this invention 0.001 % of the weight to 2% of the weight. You may add independently and these surfactants can also be added in some combination.

[0056] In manufacture of a precision integrated circuit device etc., on substrates (example: transparence substrates, such as silicon / diacid-ized silicon leather \*\*, a glass substrate, and an ITO substrate etc.), the negative-resist constituent of this invention can be applied, it can irradiate by the ability using electron-beam-lithography equipment next, and the pattern formation process to a resist film top can form a good resist pattern heating, development, a rinse, and by drying. As a developer of the negative-resist constituent of this invention A sodium hydroxide, a potassium hydroxide, a sodium carbonate, a sodium silicate, Inorganic alkali, such as a meta-sodium silicate and aqueous ammonia, ethylamine, Secondary amines, such as primary amines, such as n propylamine, diethylamine, and G n butylamine Tertiary amines, such as triethylamine and methyl diethylamine, dimethylethanolamine, The water solution of alkali, such as annular amines, such as quaternary ammonium salt, such as alcoholic amines, such as a TORIETA no amine, tetramethylammonium hydroxide, tetraethylammonium hydroxide, and a choline, a pyrrole, and a piperidine, can be used. Furthermore, surfactants, such as alcohols, such as isopropyl alcohol, and the Nonion system, can also be used for the water solution of the above-mentioned alkali, carrying out suitable amount addition. the inside of these developers — desirable — quaternary ammonium salt — they are tetramethylammonium hydroxide and a choline still more preferably.

[0057]

[Example] Hereafter, although an example explains this invention to a detail further, thereby, the contents of this invention are not limited.

1. Composition of synthetic example (1) acid-generator 1 Pentough Rollo benzenesulfonic acid tetramethylammonium salt of configuration material Pen TAFURORO benzenesulphonyl chloride 25g was dissolved in bottom methanol of ice-cooling 100ml, and 100g of tetramethylammonium hydroxide water solutions was slowly added to this 25% of the weight. When stirred at the room temperature for 3 hours, the solution of the Pentough Rollo benzenesulfonic acid tetramethylammonium salt was obtained. This solution was used for the salt exchange with sulfonium salt and iodonium salt.

[0058] 2) Synthetic diphenyl sulfoxide 50g of triphenylsulfonium Pentough ROROBENZEN sulfonate was dissolved in benzene 800ml, 200g of aluminum chlorides was added to this, and it flowed back for 24 hours. Ice 2L was slowly filled with reaction mixture, 400ml of concentrated hydrochloric acid was added to this, and it heated at 70 degrees C for 10 minutes. After washing and filtering this water solution by 500ml of ethyl acetate, what dissolved 200g of ammonium iodide in 400ml of water was added. When ethyl acetate washed after rinsing, \*\*\*\* and, and the fine particles which deposited were dried, 70g of triphenylsulfonium iodide was obtained. Triphenylsulfonium iodide 30.5g was dissolved in methanol 1000ml, 19.1g of silver oxides was added to this solution, and it stirred at the room temperature for 4 hours. The solution was filtered and the solution of the Pentough Rollo benzenesulfonic acid tetramethylammonium salt of an excessive amount was

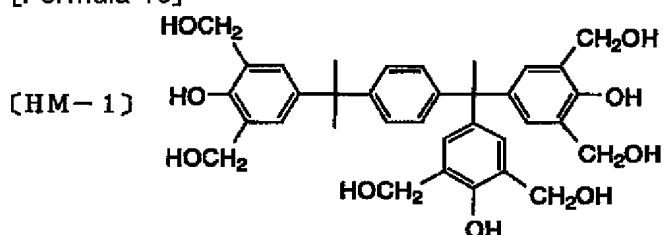
added to this. Reaction mixture was condensed, this was dissolved in dichloromethane 500ml, and a tetramethylammonium hydroxide water solution and water washed this solution 5% of the weight. When the organic phase was condensed after desiccation with anhydrous sodium sulfate, triphenylsulfonium Pentough ROROBENZEN sulfonate (I-1) was obtained.

[0059] 3) Synthetic t-amyl benzene 60g [ of JI (4-t-amyl phenyl) iodonium Pentough ROROBENZEN sulfonate ], 39.5g [ of potassium iodates ], 81g [ of acetic anhydrides ], and dichloromethane 170ml was mixed, and 66.8g of bottom concentrated sulfuric acid of ice-cooling was slowly dropped at this. After stirring under ice-cooling for 2 hours, it stirred at the room temperature for 10 hours. 500ml of water was added to reaction mixture under ice-cooling, and when it condensed after it washed this by dichloromethane and a sodium hydrogencarbonate and water washed the extract and the organic phase, the JI (4-t-amyl phenyl) iodonium sulfate was obtained. This sulfate was added to the solution of the Pentough Rollo benzenesulfonic acid tetramethylammonium salt of an excessive amount. 500ml of water was added to this solution, and when it condensed after it washed this by dichloromethane and a tetramethylammonium hydroxide water solution and water washed the extract and the organic phase 5% of the weight, JI (4-t-amyl phenyl) iodonium Pentough ROROBENZEN sulfonate (III-1) was obtained. It is compoundable using the same approach as the above also about other compounds.

[0060] (2) Synthetic 1-[alpha-methyl-alpha-(4-hydroxyphenyl) ethyl]-4-[alpha and alpha-bis(4-hydroxyphenyl) ethyl] benzene 20g (Trisp-PA by Honshu Chemical Industry Co., Ltd.) of a cross linking agent cross linking agent [HM-1] was moreover agitated and dissolved in the 10-% of the weight potassium-hydroxide water solution. Next, 60ml of formalin aqueous solution was gradually added over 1 hour under the room temperature 37% of the weight, stirring this solution. After stirring under a room temperature furthermore for 6 hours, it acted to the dilute-sulfuric-acid water solution as \*\* people. After filtering the sludge and rinsing enough, 20g of white powder of phenol derivative [HM-1] which has the hydroxymethyl group of the following structure was obtained by recrystallizing from methanol 30ml.

[0061]

[Formula 15]

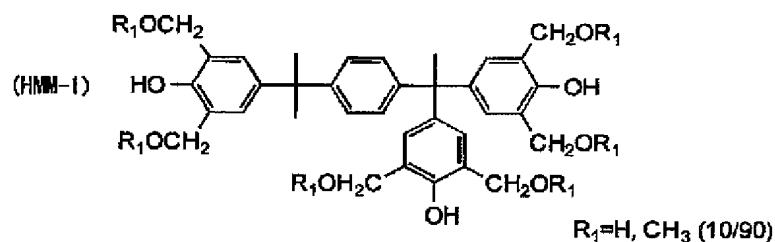


[0062] Phenol derivative [HM-1] 20g which has the hydroxymethyl group obtained in the example of the synthetic above-mentioned composition of a cross linking agent [HMM-1] was added to the 1l. methanol, and carried out heating churning, and it dissolved. Next, 1ml of concentrated sulfuric acid was added to this solution, and heating reflux was carried out for 6 hours. Reaction mixture was cooled and potassium carbonate 2g \*\* was added. After condensing this mixture enough, 300ml of ethyl acetate was added. After rinsing this solution, 18g of white solid-states of the phenol derivative [HMM-1] which has the methoxymethyl radical of the following structure was obtained by carrying out concentration hardening by drying. When asked for the rate that all the methylol radicals of a cross linking agent [HM-1] were changed

into the methoxymethyl radical with liquid chromatography, it was 70% (surface ratio), and the ratio of the methylol radical in the mixture called for from NMR and a methoxymethyl radical was 10:90.

[0063]

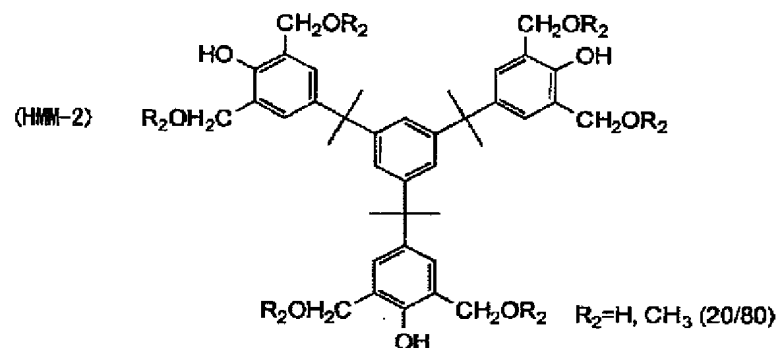
[Formula 16]



[0064] Furthermore, the phenol derivative shown below similarly was compounded.

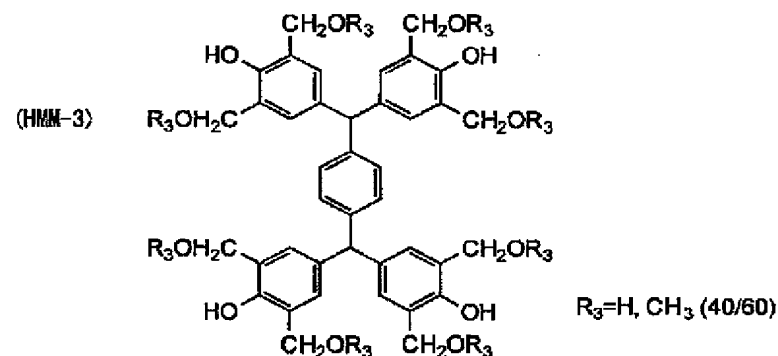
[0065]

[Formula 17]



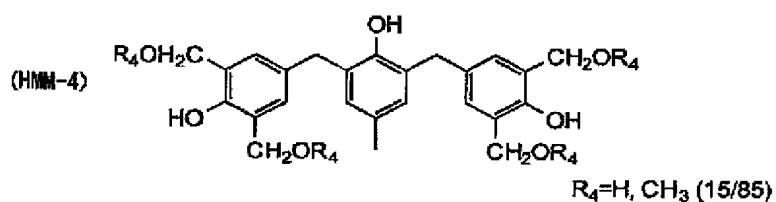
[0066]

[Formula 18]



[0067]

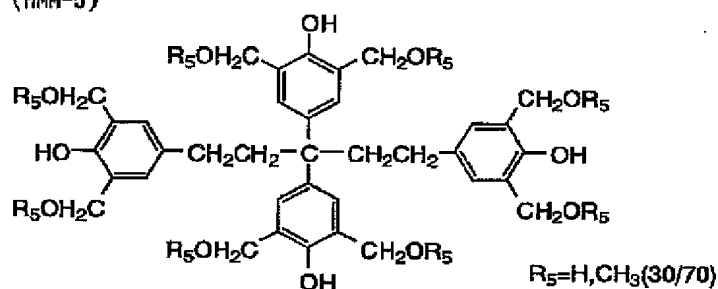
[Formula 19]



[0068]

[Formula 20]

(HMM-5)



[0069] 2. Example [Example and Example of Comparison]

(1) The resist constituent of the presentation shown in the following table 1 was filtered with the 0.1-micrometer filter using the compound and the compound for a comparison which constitute this invention chosen from the synthetic example of the painting above of a resist, and each resist solution was adjusted.

[0070]

[Table 1]

表 1

	樹 脂 (g)	酸酐生劑 (g)	架橋劑 (g)	有機塩基 (g)	有機溶劑 (g)	界面活性劑
実施例 1	P-1 (1.05)	I-1 (0.07)	HMM-1 (0.28)	TPI (0.003)	S1 ( 7.0) S4 ( 3.0)	W-1 (100ppm)
実施例 2	P-2 (1.05)	I-7 (0.07)	HMM-2 (0.28)	TPI (0.003)	S1 ( 8.6) S3 ( 2.0)	W-1 (100ppm)
実施例 3	P-1 (1.05)	I-9 (0.07)	HMM-3 (0.28)	TPI (0.003)	S1 ( 5.0) S5 ( 5.0)	W-1 (100ppm)
実施例 4	P-1 (1.05)	II-1 (0.07)	HMM-4 (0.28)	TPI (0.003)	S1 ( 9.5) S6 ( 0.5)	W-1 (100ppm)
実施例 5	P-2 (1.05)	III-3 (0.07)	HMM-5 (0.28)	TPI (0.003)	S2 ( 9.5) S7 ( 0.5)	W-1 (100ppm)
実施例 6	P-1 (1.05)	III-1 (0.07)	HMM-1 (0.28)	TPI (0.003)	S1 ( 5.0) S4 ( 5.0)	W-1 (100ppm)
実施例 7	P-1 (1.05)	III-4 (0.07)	HMM-2 (0.28)	TPI (0.003)	S1 ( 7.0) S5 ( 2.5) S6 ( 0.5)	W-1 (100ppm)
実施例 8	P-1 (1.05)	III-1 (0.07)	HMM-1 (0.28)	TPI (0.003)	S2 ( 5.0) S5 ( 5.0)	W-1 (100ppm)
実施例 9	P-2 (1.05)	PAG-1 (0.07)	HMM-4 (0.28)	TPI (0.003)	S1 ( 9.5) S8 ( 0.5)	W-1 (100ppm)
比較例 1	P-1 (1.05)	I-1 (0.07)	HMM-1 (0.28)	TPI (0.003)	S1 (10.0)	W-1 (100ppm)
比較例 2	P-2 (1.05)	I-7 (0.07)	HMM-2 (0.28)	TPI (0.003)	S1 (10.0)	W-1 (100ppm)
比較例 3	P-1 (1.05)	I-9 (0.07)	HMM-3 (0.28)	TPI (0.003)	S1 (10.0)	W-1 (100ppm)
比較例 4	P-1 (1.05)	II-1 (0.07)	HMM-4 (0.28)	TPI (0.003)	S1 (10.0)	W-1 (100ppm)
比較例 5	P-2 (1.05)	II-3 (0.07)	HMM-5 (0.28)	TPI (0.003)	S2 (10.0)	W-1 (100ppm)
比較例 6	P-1 (1.05)	PAG-2 (0.07)	CL-1 (0.28)	TPI (0.003)	S1 ( 8.0) S4 ( 2.0)	W-1 (100ppm)
比較例 7	P-2 (1.05)	PAG-3 (0.07)	CL-2 (0.28)	TPI (0.003)	S1 ( 9.5) S6 ( 0.5)	W-1 (100ppm)
比較例 8	P-1 (1.05)	PAG-2 (0.07)	CL-1 (0.28)	TPI (0.003)	S1 (10.0)	W-1 (100ppm)
比較例 9	P-2 (1.05)	PAG-3 (0.07)	CL-2 (0.28)	TPI (0.003)	S1 (10.0)	W-1 (100ppm)
比較例 10	P-1 (1.05)	I-1 (0.07)	HM-1 (0.28)	TPI (0.003)	S1 ( 7.0) S4 ( 3.0)	W-1 (100ppm)
比較例 11	P-1 (1.05)	I-1 (0.07)	PMMHMM-1 (0.28)	TPI (0.003)	S1 ( 7.0) S4 ( 3.0)	W-1 (100ppm)

[0071] The cable address used in Table 1 shows the following contents.

<Resin> P-1: Polly (p-hydroxystyrene)

Mw10,000 Mw/Mn=1.4P-2 : Novolak resin and m-cresol / p-cresol = 45/55 (mole ratio)

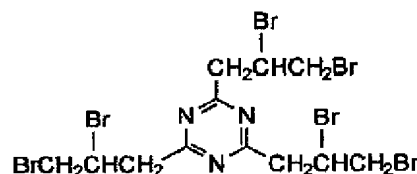
Mw6,500 [0072]

[Formula 21]

(光酸発生剤)

PAG-1 :  $\text{Ph}_3\text{S}^+ \text{CF}_3\text{SO}_3^-$ 

PAG-2 :

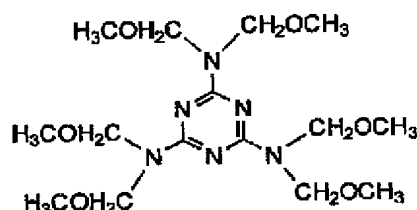
PAG-3 :  $\text{Ph}_3\text{S}^+ \text{PF}_6^-$ 

[0073]

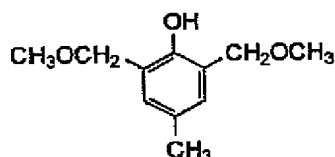
[Formula 22]

(架橋剤)

GL-1 :



GL-2 :



[0074] PMMHMM-1 : HMM-1[0075] methoxymethyl-ized completely <Organic base> TPI: 2, 4, 5-triphenyl imidazole <organic solvent> S1:propylene-glycol-monomethyl-ether acetate  
 S2:propylene-glycol-monomethyl-ether propionate S3:ethyl lactate S4:propylene-glycol-monomethyl-ether  
 S5:ethoxy ethyl propionate S6:gamma-butyrolactone S7:ethylene carbonate S8:propylene carbonate  
 S9:cyclohexanone <surfactant> W-1 : Troysol S-366 (made in Troy Chemical)

[0076] (2) the resist solution which carried out the evaluation [spreading homogeneity within substrate side] above-mentioned preparation of a resist -- the spreading machine by the canon company -- it applied on the 6 inch silicon wafer using CDR-650, and with the vacuum adsorption equation hot plate, it dried for 60 seconds and 110 degrees C of resist film of 0.300 micrometers of thickness were obtained. This resist film front face was observed with the optical microscope, it got wet, generating of the remainder and striae SHON was investigated, and each-other gap was not accepted, either. Moreover, along with the straight line which passes the thickness value of a resist along the pin center,large of a wafer by the alpha step -100 (product made from TENVCOR), ten points were measured in 1cm pitch. Distribution (mean square of a difference with an average) to the thickness of the target of the measured value was made into the index of spreading homogeneity.

[Development defect] 6 inches Bare Each resist film was applied to 0.5 micrometers on Si substrate, and 110 degrees C dried for 60 seconds with the vacuum adsorption equation hot plate. Next, after irradiating with electron-beam-lithography equipment (acceleration voltage of 50eV) through the test mask of 0.20-micrometer contact hole pattern (Hole Duty ratio = 1:3), exposure afterbaking was performed for 90 seconds at 110 degrees C. It rinsed for 30 seconds after the paddle development for 60 seconds, and with pure water by TMAH (tetramethylammonium hydroxide water solution) 2.38% of the weight succeedingly, and spin desiccation was carried out. In this way, the primary data value measured and acquired [ number / of development defects ] by KLA-2112 Made from a KEERUE ten call opportunity in the obtained sample was made into the number of development defects. The performance-evaluation result was shown in Table 2.

[0077]

[Table 2]

表 2

	塗布均一性 (A)	現像欠陥 (個)
実施例 1	5 0 以下	2 0
2	5 0 以下	3 3
3	5 0 以下	2 8
4	5 0 以下	4 5
5	5 0 以下	3 8
6	5 0 以下	4 9
7	5 0 以下	2 3
8	5 0 以下	2 9
9	5 0 以下	3 6
比較例 1	1 0 0	2 2 1
2	1 5 0	4 5 5
3	1 5 0	3 2 7
4	1 0 0	4 9 8
5	1 0 0	3 5 8
6	1 5 0	2 9 4
7	1 0 0	2 3 8
8	1 5 0	2 6 9
9	1 0 0	3 5 2
10	1 0 0	4 6 6
11	1 5 0	4 1 2

[0078] [Explanation of an evaluation result] Table 2 shows that defective generating at the time of development is also improved remarkably, while the resist constituent of this invention is excellent in the spreading homogeneity in a substrate side.

[0079]

[Effect of the Invention] By this invention, it excels in the spreading homogeneity in a substrate side, and the chemistry multiplier system negative-resist constituent for an electron ray or X-rays which mitigated defective generating at the time of development can be offered.

[Translation done.]